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Dissociation of 2,4-Bis(2,4,6-tri-*tert*-butylphenyl)-cyclo-1,3-dipnicta-2,4-diazanes (pnict = P, As, Sb) Imposed by Substituent Steric Strain: A Cyclobutane/Olefin Analogy

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Three 2,4-bis(Mes*)-cyclo-1,3-dipnicta-2,4-diazanes, **2**PnX, have been synthesized as 1,3-dichloro- (Pn = As; X = Cl) or 1,3-bis(triflato)- (Pn = P, Sb; X = OTf) derivatives (Mes* = 2,4,6-tri-*tert*-butylphenyl; OTf = triflato = trifluoromethanesulfonoxy). The compounds have been structurally characterized as cyclodimers, but spectroscopic characterization of melts and solutions indicates facile dissociation of the diphosphadiazane **2**POTf derivative to give the corresponding iminophosphine **1**POTf and of the diarsadiazane **2**AsCl derivative to give the corresponding iminoarsine **1**AsCl. 1,3-Bis(triflato)-2,4-bis(Mes*)-cyclo-1,3-distiba-2,4-diazane (**2**SbOTf) does not dissociate in the melt or in solution. The presence of the sterically bulky Mes* substituent does not preclude association of N–Pn olefin analogues to give single bonded cyclobutane analogues. The facile dissociation of **2**POTf and isolation of **1**POTf implicates a relatively high degree of substituent steric strain in the dimer. In comparison, dissociation of **2**AsCl is only apparent in the melt and in solution, likely the result of the lower substituent strain in the larger N_2As_2 framework. The largest N_2Pn_2 framework in **2**SbOTf provides sufficient space for the Mes* substituents, and the monomer is not observed under the conditions examined.

Introduction

The monomer/dimer relationship between ethene and cyclobutane classically represents the interchange of double and single carbon−carbon bonds. It has been experimentally and theoretically studied for decades and is well recognized to involve kinetically stabilized monomers that are thermodynamically unstable with respect to the dimer, enabling storage of olefin monomers and the opportunity to effect olefin polymerization on demand. While nitrogen and oxygen have a unique thermodynamic preference for NN, NO, and OO multiple bonding over single bonding, all other p-block elements mimic carbon and favor single-bonded arrangements.[1,2] Nevertheless, inorganic isolobal analogues of olefins that are suitable for polymerization are rare[3] even though a variety of polymerization processes have been developed for other inorganic species.[4,5]

The kinetic stabilization of olefins is the result of the limited orbital availability and consequential orbital-symmetry restrictions, but this is precluded for multiple bonds between heavier elements because of the accessibility of numerous unoccupied orbitals. Therefore, olefin analogues of the general formula R−N═Pn−R′ (Pn = P, As)[6,7] have only been stabilized by the presence of bulky substituents (R and R′),[6,8,9] which modify the relative monomer/dimer

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thermodynamic stability by imposition of substituent steric strain.[10] We envision the design of RNPnR′ derivatives with substituents that provide adequate steric strain for kinetic stabilization of the monomer, but with insufficient strain to enthalpically destabilize the corresponding dimer, oligomer, or polymer.

To this end, attempts to prepare derivatives of **1**PnX (Pn = P, As, or Sb; X = Cl or OTf; OTf = OSO_2CF_3; Mes* = 2,4,6-tri-*tert*-butylphenyl) have led to the isolation and characterization of the cyclodimers **2**, but we have observed an important trend in the relative stability of the monomers and dimers.

1PnX **2**PnX

Pn = P or As or Sb
X = Cl or OTf
Mes* = 2,4,6-tri-t-butylphenyl

Facile dissociation of the phosphazane derivative, **2**POTf,[11] is observed to give the corresponding iminophosphine, **1**POTf,[12] in melt and solution, and similar features are apparent for **2**AsCl. However, there is no evidence for dissociation of the antimony derivative, **2**SbOTf, under the conditions examined.

Experimental Procedures

General. Diethyl ether was obtained from ACP Chemicals Inc., and hexane was from Anachemia. All other chemicals and reagents were obtained from Aldrich Chemical Co. All solvents were degassed and stored in evacuated glass bulbs. Solids were handled in a nitrogen-filled glovebox. Sample handling and reactions were performed under oxygen- and moisture-free conditions. *n*-Butyllithium (1.6 M in hexanes) and 2,4,6-tri-*tert*-butylaniline (Mes*NH_2) were used as supplied. Dichloromethane was dried at reflux over CaH_2 and P_4O_{10}; hexane and toluene were dried over potassium, and diethyl ether was dried over sodium/benzophenone. Deuterated solvents were dried over CaH_2. PCl_3 and $AsCl_3$ were distilled, and $SbCl_3$ was sublimed in vacuo prior to use. Lithium amides were prepared under an atmosphere of nitrogen in situ by adding an equimolar quantity of ^{n}BuLi via a septum to a stirred (room temperature) solution (diethyl ether) of the amine, followed by stirring for at least 2 h. The resultant mixture was then added to the solution of trichloropnictine over a period of 15 min.

Infrared spectra were recorded as Nujol mulls on CsI plates using a Nicolet 510 FT-IR spectrometer. FT-Raman spectra were recorded on powdered samples sealed under nitrogen in melting point tubes using a Bruker RFS 100 spectrometer at 166 mW. Vibrational spectra are presented as wavenumber (cm^{-1}) maxima with ranked intensities for each absorption given in parentheses, and the most intense peak is ranked 1. Melting-point samples were placed in 1.0 mm (o.d.) Pyrex capillaries, sealed under nitrogen and measured using an Electrothermal melting-point apparatus. Elemental analyses were performed by Beller Laboratories. Solution and variable-temperature (VT) NMR spectra were recorded on a Bruker AC-250 NMR spectrometer. Solution NMR samples were flame-sealed in 5 mm Pyrex tubes. NMR spectra were referenced to the solvent and chemical shifts are reported in ppm relative to an external standard (TMS for ^{1}H and ^{13}C, 85% H_3PO_4 for ^{31}P, CCl_3F for ^{19}F).

Solid-state ^{31}P NMR spectra were obtained using Bruker double-air-bearing MAS probes on Bruker AMX-400 (9.4 T) and MSL-200 (4.7 T) spectrometers. Powdered crystalline samples were packed in 4 mm (AMX-400) and 7 mm (MSL-200) zirconium oxide rotors under an inert atmosphere. ^{31}P chemical shifts were referenced to 85% $H_3PO_{4(aq)}$ by setting the shift for solid ammonium dihydrogen phosphate ($NH_4H_2PO_4$, ADP) to 0.81 ppm. Typical rotor speeds for the MAS experiments ranged from 3 to 10 kHz. Solid-state ^{31}P CP/MAS NMR spectra were acquired with proton−phosphorus cross-polarization under conditions of Hartmann−Hahn matching.[13,14]

X-ray crystallographic data were collected on a Rigaku AFC5R diffractometer or on a Bruker P4/RA diffractometer equipped with a Smart1000 CCD detector, with graphite monochromated Mo Kα radiation for all samples except **2**AsCl, which was collected with Cu Kα radiation. Data collection was carried out at −60 °C (**2**AsCl), at −80 °C (**2**SbOTf), or at room temperature (all others). Details of the refinements are summarized in Table 1. Unit cell parameters were obtained from the setting angles of 20 to 25 high-angle reflections, except for the CCD data, where 8192 reflections were used. The choice of space group was based on systematically absent reflections and was confirmed in each case by the successful solution and refinement of the structure. During data collection for **2**POTf and **2**AsCl, the intensities of three representative reflections were measured after every 150 reflections; no decay corrections proved necessary. These data were also corrected for Lorentz and polarization effects. Secondary extinction was refined for each of the monomers but not for any of the dimers. An empirical absorption correction was applied in every case, SADABS for **2**SbOTf[15] and ψ scans for all the others. The structures were solved by direct methods (either SIR92[16] or SHELXS97[17]) and refined by full-matrix least squares using F^2 data and the program SHELXL97. A full anisotropic refinement was carried out for all structures. In all cases, the hydrogen atoms were placed in geometrically calculated positions and were allowed to ride on the heavy atom to which they were bonded with U_{iso} equal to $1.2U_{eq}$ for the heavy atom ($1.5U_{eq}$ for methyl hydrogens). The methyl carbon and hydrogen atoms of these groups were split over two positions and the occupancy of each part (A and B) refined. The carbon atoms of each A/B pair were assigned identical atomic displacement parameters. In addition, a variety of restraints had to be applied to the disordered groups to obtain reasonable results; these could include restraining the C−C bond lengths, the 1,3 C−C distances, the distances between A and B of a disordered pair, and the thermal motion of the carbon atoms. Similar restraints sometimes were also

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Table 1. Crystal Data, Data Collection, and Refinement Conditions for **1**POTf,[12] **2**POTf, **2**AsCl, **2**SbOTf, Mes*N(H)$AsCl_2$, Mes*N($SiMe_3$)$AsCl_2$, and the Decomposition Product **3**

compound label	**1**POTf [a]	**2**POTf	**2**AsCl	**2**SbOTf
molecular formula	$C_{19}H_{29}F_3NO_3PS$	$C_{38}H_{58}F_6N_2O_6P_2S_2$	$C_{36}H_{58}As_2Cl_2N_2$	$C_{38}H_{58}F_6N_2O_6S_2Sb_2$
fw	439.5	878.92	739.62	1060.48
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/n$
a (Å)	10.445(1)	11.368(2)	10.397(7)	11.4948(6)
b (Å)	10.728(1)	16.429(3)	17.611(6)	16.5251(9)
c (Å)	20.454(2)	12.013(2)	11.442(7)	12.0097(7)
β (deg)	97.78(1)	90.59(3)	113.66(4)	90.1491(10)
V (Å^3), Z	2271, 4	2243.5(7), 2	1919(2), 2	2281.3(2), 2
D_{calcd} (mg m^{-3})		1.301	1.280	1.554
R1,[b] wR2 (2σ)		0.0465, 0.0863	0.0554, 0.1191	0.0493, 0.1226
R1,[b] wR2 (all data)		0.1389, 0.0969	0.2260, 0.1738	0.0526, 0.1238
GOF[c]		1.448	1.042	1.292

compound label	Mes*N(H)$AsCl_2$	Mes*N($SiMe_3$)$AsCl_2$	**3**
molecular formula	$C_{18}H_{30}AsCl_2N$	$C_{21}H_{38}AsCl_2NSi$	$C_{18}H_{29}AsClN$
fw	406.27	478.45	369.81
cryst syst	orthorhombic	orthorhombic	monoclinic
space group	*Pbca*	*Pbca*	$P2_1/a$
a (Å)	16.412(3)	19.771(2)	12.088(2)
b (Å)	25.188(2)	19.607(2)	9.614(1)
c (Å)	10.088(3)	12.940(2)	16.7819(7)
β (deg)	90	90	107.343(6)
V (Å^3), Z	4170(1), 8	5016.3(7), 8	1861.6(3), 4
D_{calcd} (mg m^{-3})	1.294	1.267	1.319
R1, wR2 (2σ)[b]	0.0442, 0.1169	0.0349, 0.0870	0.0364, 0.0919
R1, wR2 (all data)[b]	0.1551, 0.1560	0.1299, 0.1138	0.0949, 0.1101
GOF[c]	0.999	1.013	1.016

[a] CCDC ref code LAGSUH. [b] $R1 = \sum(||F_o| - |F_c||)/\sum|F_o|$; $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$. [c] $GOF = \{\sum[w(F_o^2 - F_c^2)^2]/(n - p)\}^{1/2}$.

Table 2. Comparison of Selected Bond Distances (Å), Selected Bond Angles (deg), Sums of Angles at Selected Centers, Displacement of C_{ipso} from the Plane of the Other Five Aromatic Carbon Centers, and the Twist of the Best Aromatic Plane with Respect to the N_2Pn_2 Plane for Compounds **2**POTf, **2**AsCl, and **2**SbOTf

	1POTf[25]	**2**POTf	**2**AsCl	**2**SbOTf
N−Pn	1.477(5)	1.716(4)	1.840(8)	2.019(5)
		1.723(4)	1.855(7)	2.030(5)
Pn−X	1.926(4)	1.787(3)	2.235(4)	2.140(4)
N−Pn−N	−	82.9(2)	80.4(3)	79.3(2)
Pn−N−Pn	−	97.1(2)	99.6(3)	100.7(2)
N−Pn−X	107.8(2)	95.8(2)	104.5(3)	96.8(2)
				90.9(2)
C−N−Pn	176.4(4)	140.5(3)	140.2(6)	142.1(4)
		119.8(3)	117.8(6)	113.4(4)
∑ N angles	−	357.4(8)	356.3	356(1)
C_{ipso} − disp	−	0.173(7)	0.20(1)	0.20(1)
twist	−	67.4	62.3	67.4

applied to the phenyl ring and/or to the nondisordered butyl groups of the Mes* ligand in all of the structures.

Preparative Procedures and Characterization Data. All compounds described below have been characterized by single-crystal X-ray crystallography, as described above and data are presented in Tables 1 and 2.

Mixture of 1POTf and 2POTf. Using a variation of a previously reported[12] method, we combined **1**PCl (prepared by the reported method[18]) (0.77 g, 2.4 mmol) and AgOTf (0.65 g, 2.5 mmol) in hexane (50 mL) in one compartment of a two compartment reactor equipped with a fine glass filter. After the mixture was stirred for 4 days in the dark, the orange reaction mixture was filtered into the second compartment. The removal of solvent under static vacuum over a period of 2 days left a mixture of large orange crystals and small yellow crystals, which were washed with solvent by cold-spot back distillation. Total Yield: 0.85 g, 82%. Anal. Calcd for $C_{19}H_{29}F_3NO_3PS$ (found): C, 51.93 (51.20); H, 6.65 (7.09); N, 3.19 (3.09). A sample of each type of crystal was isolated by manual separation. Orange crystals were assigned as **1**POTf on the basis of X-ray crystallographic analysis. mp: 124−126 °C. FT-IR: 1599-(9), 1464(1), 1398(15), 1366(3), 1266(14), 1235(7), 1196(6), 1184-(5), 1150(4), 1134(11), 914(2), 886(10), 629(8), 585(12), 532(13). FT-Raman: 2971(2), 2911(3), 1598(4), 1475(1), 1368(12), 1292-(13), 1266(14), 1203(8), 1134(5), 1070(6), 926(15), 823(7), 781-(11), 764(10), 571(16), 103(9). Yellow crystals were assigned as **2**POTf on the basis of X-ray crystallographic analysis. d.p.: 113 °C (color change to orange). For the resulting orange solid, the melting point was 124−126 °C, and the IR data were consistent with those of **1**OTf above. FT-IR: 1598(14), 1462(2), 1408(3), 1363(6), 1241(7), 1208(1), 1142(5), 1101(8), 1027(15), 916(13), 884(9), 827(4), 755(11), 638(12), 602(10). FT-Raman: 3016(17), 2973(1), 2914(2), 1598(4), 1468(13), 1447(12), 1230(8), 1206(9), 1152(10), 1029(11), 925(16), 824(3), 767(15), 568(7), 139(5), 117-(6), 83(14).

NMR of crystal mixture (δ) (CD_2Cl_2): ^{31}P 50.1; ^{19}F −78.3; ^{1}H 1.32 (s, 9H, *p*-^{t}Bu), 1.49 (s, 18H, *o*-^{t}Bu), 7.42 (s, 2H, Ar−H); ^{13}C-{^{1}H} 29.9, 31.1, 33.9, 36.2, 98.9, 123.1, 135.7, 140.0, 150.7; ^{31}P (in Et_2O) 51.4, (in CH_2Cl_2) 50.0 (an additional low intensity signal at 137 is assigned to **1**PCl), (in toluene) 51.7, (reaction mixture in hexane) 55.9. The all-solution ^{31}P NMR spectra show an additional low-intensity unassigned peak at 279 ppm.

The ^{31}P chemical shift tensors of the phosphorus nuclei of the monomer (**1**POTf) and dimer (**2**POTf) were characterized by spinning samples at the magic angle at several different speeds. A Herzfeld−Berger analysis[19] of the spinning sidebands yielded the following principal components: monomer (**1**POTf) $\delta_{11} = 226$ ppm, $\delta_{22} = 202$ ppm, $\delta_{33} = -277$ ppm, $\delta_{iso} = 50$ ppm; dimer (**2**POTf) $\delta_{11} = 460$ ppm, $\delta_{22} = 318$ ppm, $\delta_{33} = -5$ ppm, $\delta_{iso} = 258$ ppm The estimated error in the principal components of the phosphorus

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chemical shift tensors is ±5 ppm. DFT/B3LYP quantum chemistry computations are in reasonable agreement with experiment.

Mes*(H)NAsCl$_2$. Mes*NH$_2$ (3.93 g, 15.0 mmol), ^{n}BuLi (15 mmol), AsCl$_3$ (>1.5 mL, >17 mmol) in diethyl ether (15 mL) were combined at room temperature (as outlined in the general procedures) producing a purple solution and a white precipitate. The solution was pink after 3 days; it was was filtered, and solvent was removed from the filtrate in vacuo to leave a peach crystalline material. Yield: 5.8 g, 95%. An elemental analysis was not performed. mp: 60−65 °C. FT-IR: 3520(33), 3453(30), 3406sh-(21), 3386(11), 3095(25), 3032(16), 2744(29), 1768(28), 1620(23), 1598(13), 1558(26), 1434sh(8), 1420(4), 1393, 1361(1), 1286(14), 1265(15), 1240(6), 1216(3), 1201sh(10), 1190sh(12), 1022(32), 928-(31), 913(34), 880(5), 843(9), 816(19), 792(22), 769(27), 757(18), 723(35), 642(20), 547(36), 466(24), 361(2), 332sh(7), 281(17). NMR (δ): ^{1}H (CD$_2$Cl$_2$) 1.30 (s, 9H, *p*-^{t}Bu), 1.51 (s, 18H, *o*-^{t}Bu), 5.48 (broad s, 1H, N−H), 7.38 (s, 2H, Ar−H).

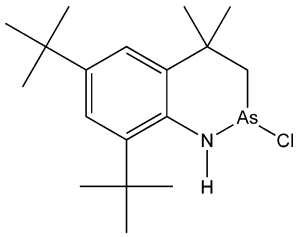
Mes*(Me$_3$Si)NAsCl$_2$. Mes*N(SiMe$_3$)H (0.73 g, 2.2 mmol) in diethyl ether (20 mL), ^{n}BuLi (2.2 mmol), and AsCl$_3$ (1 mL, >12 mmol) in diethyl ether (20 mL) were combined as outlined in the general procedures and stirred at room temperature for 8 h. The solution was filtered, and the removal of solvent in vacuo left a crystalline material surrounded by a viscous oil, which was recrystallized from hexane by slow evaporation (1 day) to give yellow crystals. Yield: 0.19 g, 19%. Anal. Calcd for $C_{21}H_{38}AsCl_2$-NSi (found): C, 52.72 (53.03); H, 8.01 (8.02); N, 2.93 (2.96). mp: 109−111 °C. FT-IR: ∼3685v.br(18), 3280(28), 3231(33), 3087-(34), 3065(35), 1601(30), 1403sh(16), 1391(8), 1389(11), 1256-(7), 1254(9), 1213(14), 1168(13), 1196(23), 1134(32), 1089(22), 1092(3), 1019(24), 908(26), 883(5), 855br(1), 841br(2), 773(15), 762(12), 751(10), 742(8), 695(20), 676(21), 636(19), 546(25), 477-(19), 458(30), 428(31), 379(21), 364(4), 347(27), 321(6). NMR (δ): $_1$H (CD$_2$Cl$_2$) 0.25 (s, 9H, SiMe$_3$), 1.22 (s, 9H, *p*-^{t}Bu), 1.48 (s, 18H, *o*-^{t}Bu), 7.42 (s, 2H, Ar−H); (THF-D8) 0.34 (s, 9H, SiMe$_3$), 1.31 (s, 9H, *p*-^{t}Bu), 1.56 (s, 18H, *o*-^{t}Bu), 7.53 (s, 2H, Ar−H).

2AsCl. NEt$_3$ (10 mL) in Et$_2$O (15 mL) was added to Mes*(H)-NAsCl$_2$ (1.36 g, 3.34 mmol) in Et$_2$O (15 mL), producing a dark purple solution and a white precipitate. The mixture was filtered, and the volatiles were removed in vacuo from the filtrate to leave a yellow solid. The compound was extracted with hexane and filtered (to remove any remaining NEt$_3$HCl), and the solvent was removed by distillation. The resulting solid was recrystallized from Et$_2$O over a period of one week, during which the solution temperature was maintained below 10 °C. Yellow crystals. Yield: 0.250 g, 20%. Anal. Calcd for $C_{19}H_{29}AsClN$ (found): C, 58.46 (59.04); H, 7.90 (8.08); N, 3.79 (3.75). mp: 159−164 °C (color change to red at 105 °C). FT-IR: 2624(29), 2606(28), 2533(43), 2499(38), 1597(24), 1409(9), 1398(7), 1392(10), 1363(3), 1291-(22), 1262(16), 1241(14), 1201(6), 1188(12), 1175(5), 1141(31), 1104(1), 1037(33), 1027(34), 947(44), 933(37), 912(18), 879(11), 847(2), 819(27), 801(4), 756(17), 751(20), 731(8), 650(39), 635-(19), 591(32), 548(23), 539(36), 482(21), 458(42), 412(35), 370-(15), 321(13), 303(40), 293(26), 291(25). NMR (δ): ^{1}H (CD$_2$Cl$_2$) 1.31 (s, 9H, *p*-^{t}Bu), 1.62 (s, 18H, *o*-^{t}Bu), 7.37 (s, 2H, Ar−H).

The storage of **2**AsCl in solution above 10 °C resulted in precipitation of a crystalline material that was structurally characterized (see Table 1) as isomer **3**.

NMR (δ): ^{1}H (CD$_2$Cl$_2$) 1.32 (s, 9H, *p*-^{t}Bu), 1.46, 1.47 (overlapping s, 15H total, 4-^{t}Bu, 2-CMe$_2$), 2.47 (broad m, 2H, CH$_2$−As), 5.95 (broad s, 1H, N−H), 7.28 (d, $^4J_{H-H}$ = 2.14 Hz, Ar−H), 7.32 (d, $^4J_{H-H}$ = 2.14 Hz, Ar−H).

2SbOTf. A mixture of Mes*NH$_2$ (4.93 g, 18.9 mmol) and ^{n}-BuLi (18.9 mmol) in toluene (30 mL) was added to a solution of



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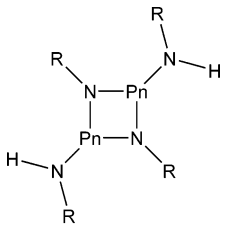
SbCl$_3$ (2.19 g, 9.60 mmol) in toluene (20 mL) over a period of 10 min at −78 °C. After 3 h, the yellow solution was warmed to room temperature, filtered, and added to AgOTf (2.50 g, 9.73 mmol) in toluene (20 mL). After 15 min, the orange solution was filtered from the white precipitate and left to stand in the dark for several days to produce orange crystals. Yield: 1.53 g, 15%. Anal. Calcd for $C_{19}H_{29}F_3NO_3SSb$ (found): C, 43.04 (42.92); H, 5.51 (5.59); N, 2.64 (2.73). mp: remains solid above 360 °C. FT-IR: 1599-(22), 1588(27), 1568(37), 1515(33), 1424(13), 1398(18), 1367(12), 1363(11), 1312(10), 1295(6), 1269(4), 1245(5), 1229(1), 1186(7), 1182(8), 1157(0), 1109(14), 1078(29), 1022(2), 964(26), 942(25), 915(30), 879(20), 856(17), 821(35), 804(34), 784(36), 765(21), 756-(23), 733(19), 704(28), 694(31), 670(32), 646(16), 635(3), 576-(24), 519(15), 470(28), 353(39). NMR (δ): ^{1}H (CD$_2$Cl$_2$) 1.30 (s, 9H, *p*-^{t}Bu), 1.65 (s, 18H, *o*-^{t}Bu), 7.41 (s, 2H, Ar−H).

Results and Discussion

Facile dehydrochloride coupling reactions occur between primary amines and trichloropnictines to give aminopnictines, but the isolation of the amination products is complicated by the coincident formation of monoaminodichloro-, diaminochloro-, and trisaminopnictines,[20,21] as well as the possibility for formation of iminopnictines (derivatives of **1**) and cyclo-1,3-dipnicta-2,4-diazanes (derivatives of **2**). The formation of specific aminopnictine (or iminopnictine) products can be enhanced by the presence of substituents on the amine that possess appropriate steric bulk and by the use of lithium amide reagents rather than amines. For example, the reaction of PnCl$_3$ with LiN(H)Dipp provides the corresponding 1,3-diamino-cyclo-1,3-dipnicta-2,4-diazane, **4** (R = Dipp = 2,6-diisopropylphenyl), for all heavy pnictogens (Pn = P, As, Sb and Bi).[21]



4

Analogous reactions involving LiN(H)Mes*, containing a bulkier substituent, give the aminoiminopnictine **5** (R = Mes* = 2,4,6-tri-*tert*-butylphenyl) for Pn = P or As[7] and the trisaminopnictine **6** (R = Mes*) for Pn = Sb or Bi.[22]

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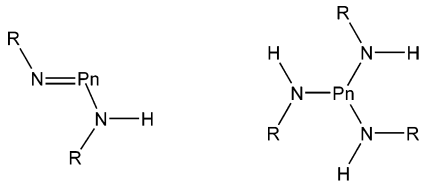

5 **6**

These subtle differences in the stoichiometry of pnictine amination imposed by small adjustments in substituent steric bulk prompted us to assess the influence of a single Mes* substituent for each N−Pn unit on the relative stability of the monomer (**1**) and dimer (**2**). We anticipate that the appropriate selection and combination of substituents will provide relative kinetic stability for the monomer and a relative thermodynamic preference for oligomers that ultimately allows controlled association as polymers.

The dimeric compounds **2**POTf, **2**AsCl, and **2**SbOTf have been prepared using conventional synthetic methodologies. They have been comprehensively characterized, and the solid state structures have been confirmed by X-ray crystallography (Tables 1 and 2 and Figure 1). All three show a characteristic four-membered, essentially square Pn_2N_2 core, with almost planar nitrogen centers and pyramidalized pnictogen centers that adopt an anti configuration for their exocyclic substituents.

As previously reported,[18,23] the iminophosphine monomer **1**PCl is readily obtained in the reaction of PCl_3 with NH_2-Mes* in the presence of excess NEt_3. The corresponding dimer **2**PCl has not been observed. The triflate derivative **1**POTf is quantitatively formed in the equimolar reaction mixture of **1**PCl with AgOTf,[12] and it was first isolated as an orange crystalline solid by storage for hours at −30 °C under Schlenk conditions at ambient pressure.[12] However, when a hexane solution of **1**POTf was slowly evaporated at room temperature (20 °C), under reduced pressure (10^{-3} Torr), a mixture of orange and yellow crystals was obtained; they have been characterized as the monomer **1**POTf and the dimer **2**POTf, respectively.[11] Spectroscopic and crystallographic data for the orange crystals are consistent with those originally reported for **1**POTf,[12] and the solid-state structure of the yellow crystals has been confirmed to be **2**POTf by X-ray crystallography (Table 1). The cell parameters for a number of crystal samples of each (**1**POTf and **2**POTf) have been determined to confirm the characterization of each bulk material.

When heated, the crystals of **2**POTf change color (yellow to orange) and then melt at the same temperature as the crystals of **1**POTf. The cooled melt exhibits all of the distinct IR features of **1**POTf, indicating that the monomer is readily formed from the dimer in the solid state or during the melting process. ^{31}P NMR spectra of solutions prepared by the solvation of **2**POTf in a variety of solvents revealed the presence of only **1**POTf, indicating quantitative dissociation of the dimer in solution.

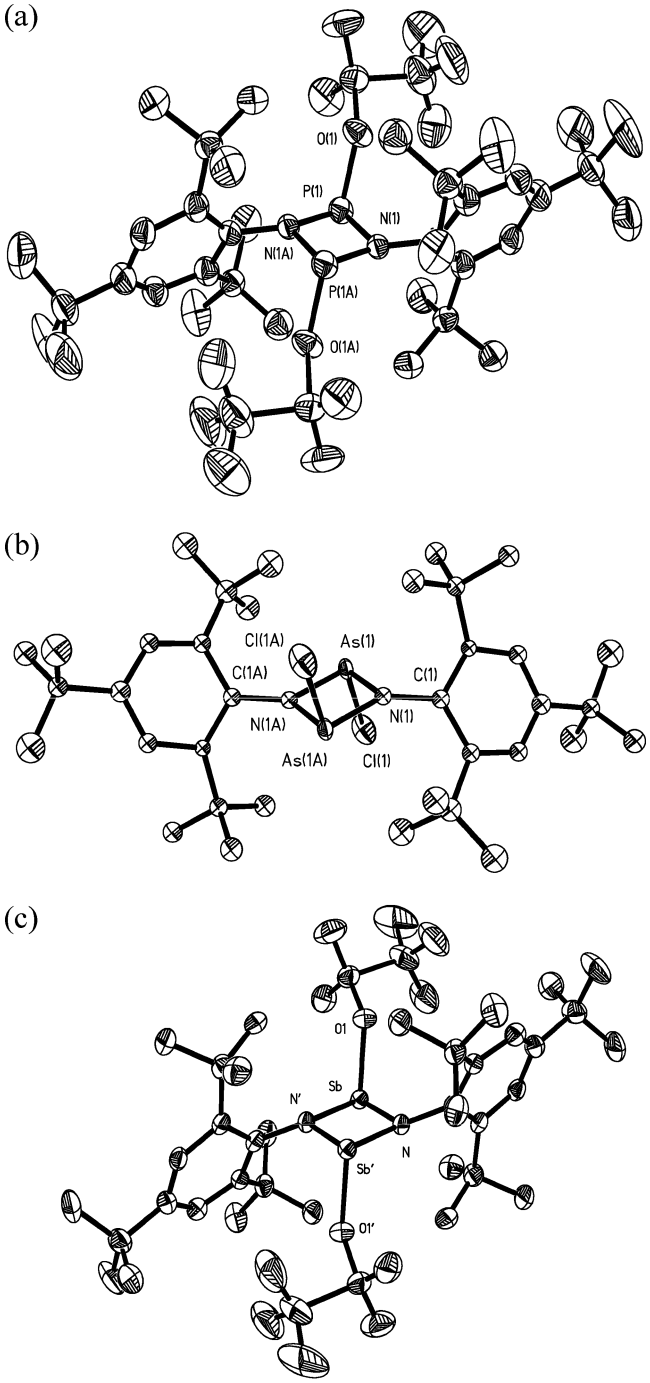

Figure 1. Structural views of (a) **2**POTf, (b) **2**AsCl, and (c) **2**SbOTf.

The molecular structure of **2**POTf (Figure 1a) has a square N_2P_2 core with crystallographically indistinguishable N−P distances [1.716(4) and 1.723(4) Å] that are in the typical range for derivatives of cyclo-1,3-diphospha-2,4-diazanes.[24] The N−P distances in **2**POTf are substantially longer than that in the solid-state structure of the monomer **1**POTf [1.477(5) Å],[12] consistent with a cyclobutane/ethene (single bond/double bond) analogy. The difference in the P−O distances of **1**POTf [1.926(4) Å][12] and **2**POTf [1.787(3) Å]

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implies a higher degree of ionicity for the monomer that is corroborated by the more uniform distribution of S−O bond lengths in **1**POTf [1.499(4), 1.405(4), and 1.409(4) Å][12] than in **2**POTf [1.549(3), 1.409(4), and 1.424(4) Å]. The P−N−P [97.1(2)°] and N−P−N [82.9(2)°] angles are also typical for cyclo-1,3-diphospha-2,4-diazanes.[24] The C−N−P angles in **2**POTf [140.5(3) and 119.8(3)°] are necessarily smaller than the nearly linear C−N−P angle [176.4(4)°] in **1**POTf,[12] and the C−N bond [1.467(6) Å] is significantly longer than the one in **1**POTf [1.386(7) Å],[12] suggesting a distinction in the degree of π interaction between the NP core and the aromatic frame of the 2,4,6-tri(*tert*-butyl)phenyl substituent. In this context, the Raman spectrum of **2**POTf is much less intense than that of **1**POTf, which exhibits an intense N−P stretch at 1464 cm^{-1} consistent with a highly polarizable, essentially linear, geometry that allows for conjugation with the Mes* aromatic system.[25]

The facile synthesis of **1**PCl from PCl_3 and NH_2Mes* in the presence of excess NEt_3[18,23] was not successfully extrapolated to the analogous mixture of $AsCl_3$ and NH_2-Mes*. Nevertheless, the **2**AsCl dimer has been prepared via a sequential synthetic study that included the isolation of Mes*N(H)$AsCl_2$ from the reaction of LiN(H)Mes* and $AsCl_3$ and the isolation of Mes*N($SiMe_3$)$AsCl_2$ from the reaction of LiN($SiMe_3$)Mes* and $AsCl_3$. These two aminodichloroarsines exhibit predictable spectroscopic and solid-state (crystallographic) structural features (Table 1). Dehydrochlorination of the secondary amine Mes*N(H)$AsCl_2$, using excess NEt_3, resulted in a purple solution that precipitated the **2**AsCl dimer as a yellow crystalline solid (Figure 1b). It has not been possible to isolate **1**AsCl or **2**PCl with similar or modified crystal-growth conditions or alternative solvents. Attempts to prepare **2**AsOTf from **2**AsCl using AgOTf have not been successful.

Samples of **2**AsCl exhibit distinct color changes under different conditions. Before melting at 159−164 °C, the yellow solid becomes red at 105 °C. In donor solvents (such as Et_2O), an initially yellow solution slowly (5−10 min) changes to red. After the solution was cooled and the solvent was removed under vacuum, a yellow solid was isolated and characterized as the **2**AsCl dimer. In light of the orange-red colors documented for iminophosphines and iminoarsines,[7] we speculate that **2**AsCl dissociates to **1**AsCl reversibly in solution.

The silylaminoarsine Mes*N($SiMe_3$)$AsCl_2$ was thermolyzed under a variety of conditions with the expectation of silyl chloride elimination; however, the ^{1}H NMR spectra of the reaction mixtures were complicated. Crystalline material isolated from thermolysis experiments has been characterized by X-ray crystallography and NMR spectroscopy as compound **3**, a bicyclic isomer of **1**AsCl, formally resulting from the intramolecular insertion of the NAs bond into a C−H bond of a methyl group of the ortho butyl substituent. Activation of the C−H bond in an ortho *tert*-butyl group has been previously observed in a variety of cases involving phosphorus[26−28] and arsenic.[29]

Neither **1**SbCl nor **2**SbCl has been isolated from the reaction between $SbCl_3$ and LiN(H)Mes*. However, the addition of AgOTf to the reaction mixture gave an orange solution, from which the cyclo-1,3-distiba-2,4-diazane **2**SbOTf has been isolated and structurally characterized in the solid state (Figure 1c). In contrast to the observations made for **2**POTf and **2**AsCl, there is no apparent color change when **2**SbOTf is solvated or heated and decomposition occurs above 360 °C without evidence of melting. Few derivatives of cyclo-1,3-dibisma-2,4-diazanes have been reported,[21,30,31] and attempts to isolate the bismuth analogues of **1** or **2** have been unsuccessful.

The structural features for the new derivatives of **2** are predictably different from those N_2P_2 heterocycles,[24] N_2As_2 heterocycles[32,33] and N_2Sb_2 heterocycles[34−41] involving higher coordination numbers for the pnictogen center, but are consistent with those of cyclo-1,3-diphospha(III)-2,4-diazanes,[24] cyclo-1,3-diarsa(III)-2,4-diazanes,[21,42−45] and cyclo-1,3-distiba(III)-2,4-diazanes,[21,46−51] respectively. The struc-

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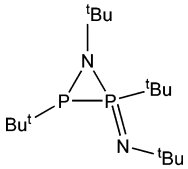
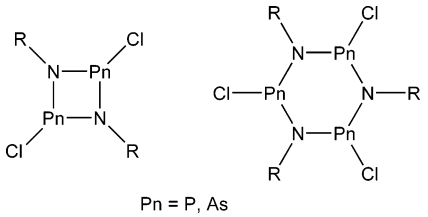
tural features (Table 2) of all three new derivatives are surprisingly similar. The planar N_2Pn_2 framework includes essentially planar nitrogen centers (cf. the sum of the N angles is almost 360°) with the substituents at the pnictogen center adopting an anti configuration. The twist angles of the aromatic best plane of the Mes* substituent with respect to the N_2Pn_2 plane are very similar (67.4, 62.3, and 67.4°), indicating that the steric presence of the Mes* substituent at nitrogen has minimal influence on the structure of the cyclodipnictadiazane. Therefore, the substituent steric strain is accommodated by deformation of the aromatic ring at the ipso carbon atom, which is displaced from the plane of the other five aromatic centers by a similar degree in all three compounds (Table 2, C_{ipso} − disp).

The facile dissociation of **2**POTf and **2**AsCl indicates a small thermodynamic distinction between dimer and monomer in each case consistent with a cyclobutane/olefin-like interchange. Such equilibria have been previously recognized for NP compounds,[52] although the dimer is sometimes characterized as a nonsymmetric P−P−N triangular framework (e.g., **7**).[53,54]



7

Also relevant are the proposed elimination of an iminophosphine unit from a trimeric heterocycle on the basis of spectroscopic data,[55] and the dissociation of the cyclo-1,3-dipnicta-2,4-diazane **8** (Dmp = 2,6-dimethylphenyl; Dipp = 2,6-diisopropylphenyl) as part of the ring expansion reaction to derivatives of **9**.[56,57]



8 Pn = P, As; R = Dmp, Dipp **9**

Conclusions

The iminophosphine, **1**POTf, and corresponding dimer, **2**POTf, have been crystallized simultaneously from solution at room temperature, showing that the presence of the sterically bulky Mes* substituent does not preclude the association of N−P olefin analogues to produce single-bonded cyclobutane analogues. Analogous dimers **2**AsCl and **2**SbOTf, containing the heavier pnictogens, have been prepared and characterized. While the phosphorus derivative, **2**POTf, dissociates to the monomer in the melt and in solution and the arsenic derivative, **2**AsCl, is speculated to dissociate in solution on the basis of a dramatic reversible color change, the antimony derivative, **2**SbOTf, shows no evidence of dissociation, indicating the accommodation of substituent steric strain by the larger N_2Sb_2 framework.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada, the Killam Foundation, the Canada Research Chairs Program, the Canada Foundation for Innovation, the Nova Scotia Research and Innovation Trust Fund, and the Walter C. Sumner Foundation for funding. We also thank Andrew D. Phillips for collecting some of the experimental data and the Atlantic Region Magnetic Resonance Centre for use of instrumentation.

Supporting Information Available: Crystallographic information files (CIF) for all of the compounds presented above. This material is available free of charge via the Internet at http://pubs.acs.org.

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